bringing the calculated[16] yields into line with experiment.

The transmission coefficient of the surface barrier is an important factor in the description of photoelectric emission, and experiments such as that described, which could provide definite information on the barrier transmission coefficient, would be of great value, particularly as the special barriers assumed by certain authors to explain the normal and total energy distributions are very different, both from each other and from the theoretical barrier for an "ideal" metal.

The writer wishes to record his indebtedness to Dr. R. E. B. Makinson, who suggested this investigation, for many helpful discussions during its progress.

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[16] R. E. B. Makinson, Proc. Roy. Soc. **A910**, 367 (1937).

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The Mechanism of Self-Diffusion in Alkali Metals

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On the basis of calculations of the activation energies of various ring, vacancy, and interstitial mechanisms in alkali metals, the most probable mechanism of self-diffusion is found to be the rapid transmission of short linear regions of compression (referred to as "crowdions") along body-diagonals in the body-centered cubic lattice. The creation of crowdions, which can be regarded as interstitial atoms diluted over a region of about eight interatomic distances in a vernier-like fashion, occurs at the surface rather than in the interior of a perfect lattice. The calculation of the corresponding energy of formation depends on the empirical values for the work function, heat of sublimation, and ionization energy; for sodium, the total heat of activation for diffusion by crowdions is probably less than one-tenth of one electron volt.

I. INTRODUCTION

DIFFUSION in a periodic structure, such as a crystal lattice without macroscopic faults, is presumably the result of a large number of elementary steps from one stable configuration to the next equivalent one. While any elementary mechanism will in general involve the displacement of many atoms in the saddle point configuration (relaxation of neighboring atoms), we may distinguish between elementary steps resulting in the net displacement of one or of several atoms. The former type is only possible if we have either an interstitial atom or a vacancy in the lattice, while an example of the latter process is the cyclic interchange of two or more atoms, which would be the mechanism of self-diffusion in a perfect lattice. The exchange of two neighboring atoms in a metallic lattice is energetically unlikely because of their mutual repulsion. However, Zener[1] suggested that cyclic interchange of more than two atoms in a ring would reduce the activation energy required (due to mutual repulsion). Such steps involving the net displacement of many atoms are not energetically unlikely when the displacements of the individual atoms produce forces aiding the over-all motion. Huntingdon and Seitz[2,3] showed that in the case of copper a vacancy mechanism is probably dominant in accounting for the measured activation energy for self-diffusion.

The alkali metals present a structure which can be approximated by a particularly simple model of positive point charges embedded in a uniform negative charge density. Calculation of the activation energy of various elementary mechanisms in this model can be carried out rigorously involving essentially long-range Coulomb forces. It is found that insertion of an interstitial atom requires much less energy than in the case of copper,[2] where we have neighboring-shell-repulsion to contend with. The energetically favorable interstitial position is not, however, the geometrically obvious face center of the body-centered cubic structure, but between nearest neighbors, the insertion being accompanied by very considerable relaxation displacement along that line of nearest neighbors (forming the stable "crowdion" configuration). The elementary step in the diffusion process involves, then, the net displacement of about eight atoms forming the crowdion,[4] and requires very little activation energy of migration, due to the cooperative action of the several dipoles corresponding to the individual displacements of the ions. Vacancy and ring mechanisms are found to require much higher energies of formation and migration respectively.

The model adopted is a body-centered cubic lattice of positive point charges (each of one electronic charge in magnitude) embedded in a homogeneous negative charge density of constant value balancing the positive

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[1] C. Zener, Acta Crys. **3**, 346 (1950).
[2] H. B. Huntingdon and F. Seitz, Phys. Rev. **61**, 315 (1949).
[3] F. Seitz, Acta Crys. **3**, 355 (1950).
[4] The term "crowdion" has been coined as a descriptive designation for a short linear region of compression.

charges. We are thus neglecting the finite size of the sodium ion core, and the increase in "free electron" density in the immediate neighborhood of the nucleus. Fuchs[5] has shown that this approximation introduces an error of about ten percent in the elastic constants for sodium. Allowing for relaxation of the electron distribution in the course of motion of the ions would always lower the activation energy, which is here calculated assuming a rigid uniform negative charge distribution throughout.

We designate by $2a$ the side of a cubic unit cell; for sodium, $a=2.12\times10^{-8}$ cm, and $e^2/a=6.80$ ev (where e is the electronic charge).

In the perfect lattice the least energy required for the simultaneous creation of a vacancy and an independent interstitial atom in the interior (allowing for relaxation in position of surrounding ions) was found to be about $0.6\,e^2/a$ corresponding to an activation energy of $0.3\,e^2/a$ for production of one vacancy. To avoid the necessity for creation of such vacancies and interstitial atoms, we might consider the alternate mechanism for diffusion, the cyclic interchange of atoms.

II. RING MECHANISMS

The most favorable ring mechanism involved the cyclic exchange of four nearest neighbors in a plane, and requires an activation energy of $0.24\,e^2/a$. The detailed results, involving the calculation of potentials by the Ewald method,[6] are as follows:

(a) self-potential at lattice point: $-1.820\,e/a$,
(b) hence, the energy required to remove 4 nearest neighbors to points of zero potential infinitely far apart: $+10.44\,e^2/a$,
(c) potential at point midway between nearest neighbor lattice points: $-0.200\,e^2a$.
(d) energy of repulsion for four ring atoms at midpoints, per atom: $+1.142\,e^2/a$,
(e) energy of attraction by holes created at lattice points ("hole effect") per atom at mid point: $-3.371\,e^2/a$,
(f) hence, energy of activation for plane undistorted 4-atom ring: $0.70\,e^2/a$.

We now allow the ring to be distorted as it passes the half-way position; it is found that buckling of the ring out of the plane, or symmetric distortion in the plane along the equilibrium direction of the sides of the ring does not result in an appreciable lowering of the activation energy. On the other hand, we do gain by allowing relaxation in the position of the ions outwards from the mid-point positions. This is due to the fact that the repulsion energy term has a finite slope (when plotted against the distance from mid-point) already at the mid-point of the straight side, and therefore decreases faster at first, as we go out, than the attractive term due to the holes increases, the latter having a minimum for the undistorted position. The saddle point is found at an approximate distance of $a/4$ from the mid-point of the undistorted ring. Here we have a repulsion term of 0.875, and an attraction term of $-3.166\,e^2/a$ per atom. Strict calculation of the Ewald potentials then gives us an activation energy of $0.29\,e^2/a$.

TABLE I. Energies of various ring mechanisms.

Ring configuration	Activation energy	Repulsion energy per atom	Hole effect per atom
Undistorted plane nearest neighbor 4-ring without dipole relaxation	$0.70\,\frac{e^2}{a}$	$+1.142\,\frac{e^2}{a}$	$-3.371\,\frac{e^2}{a}$
Optimally distorted plane nearest neighbor 4-ring without dipole relaxation	0.29	+0.875	−3.166
with dipole relaxation	0.24		
Undistorted folded nearest neighbor 4-ring without dipole relaxation	1.122	+1.353	−3.516
Optimally distorted folded nearest neighbor 4-ring (dipole relaxation negligible)	0.504	+0.902	−3.155
Undistorted cube-face *r*-ring without dipole relaxation	0.85	+0.957	−2.898
Undistorted plane 6-ring (two sides $2a$, four sides $3a$ long) without dipole relaxation	1.06	+1.747	−3.585
Undistorted buckled 6-ring (6 equal obtuse angles) without dipole relaxation (effect of distortion $0.20\,e^2/a$)	0.51	+1.294	−3.906
Undistorted plane 8-ring (with 2 acute angles) without dipole relaxation	0.88	...	...
Undistorted buckled 8-ring (obtuse angles only) without dipole relaxation	0.48	...	...

Finally, we allow a group of eight and a group of four neighbors to relax simultaneously (relaxation of other ions is found to be negligible). Maximizing the energy gain, calculated in the dipole approximation for constant curvature in potential about the lattice point, we obtain a set of simultaneous linear equations for the values of the dipole displacements, and the relaxation energy is found to be $0.05\,e^2/a$, giving us a final activation energy of $0.24\,e^2/a$ for the ring motion.

These energies and those of some alternate ring mechanisms considered are listed in Table I.

It will be seen that the term corresponding to mutual repulsion of the ions in the saddle point configuration is, and hence the activation energy tends to be, reduced by avoiding acute angles in the ring.

III. LONG CHAIN MECHANISMS

This remark leads us to consider the limiting case of translation in a straight line. The energy *per atom* required for rigid translation of an infinite straight chain

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[5] K. Fuchs, Proc. Roy. Soc. **A153**, 636 (1936); **A157**, 444 (1936).

[6] M. Born and M. Goeppert-Mayer, Handbuch der Physik, **XXIV/2**, 710.

FIG. 1. Diagram of crowdion. × denotes lattice positions; ● denotes ions.

of nearest neighbors (e.g., along the 1:1:1 direction) through the mid-points saddle position was calculated as follows:

(a) Self-potential at equilibrium position: $-1.8199 \pm 0.0004\ e/a$,
(b) potential at saddle point position: $-0.2004 \pm 0.001\ e/a$,
(c) interaction (hole and repulsion effect):

$$\frac{4}{\sqrt{3}}\sum_{n=1}^{\infty}\frac{(-1)^n}{n}\frac{e^2}{a}=-\frac{4}{\sqrt{3}}(\log 2)\frac{e^2}{a}$$

$$=-1.6008\frac{e^2}{a}\ \text{per atom},$$

(d) hence, activation energy of chain shift without dipole relaxation: $0.0187\ e^2/a$ per atom,
(e) energy gain due to dipole relaxation of six neighboring chains (allowing for all three types of mutual interaction of the six claims): $0.0132\ e^2/a$ per atom.

The dipole relaxation in these neighboring chains is appreciable in spite of the small net electrostatic field acting, because of the shallow potential curvature along a chain corresponding to parallel dipole displacements.

We thus get an activation energy for rigid translation of a nearest-neighbor-chain of $0.0187-0.0132 = 0.0055\ e^2/a$ per atom.

This result, showing the ease of translation of straight chains of nearest neighbors (if it were not for the end effects resulting in an interstitial atom and a vacancy) owing to the cooperation of the parallel dipoles, suggested, first, consideration of rings formed by such chains. However, the repulsive effect (about $+0.02\ e^2/a$) at each corner, of which there must be at least 6 to avoid acute angles, did not allow this to be a favorable mechanism. The distortion relaxation was small, owing to the high potential curvature in that direction, corresponding to the shallow potential variation along the chain (the Laplacian of the potential being $\pi e/3a^3$ everywhere in the uniform negative charge distribution); similarly, it is a general result that the "better" the ring from the point of view of angles, the smaller the dipole relaxation of the surrounding atoms.

IV. THE CROWDION

However, the low energy per atom required to shift a straight chain (which only applies to nearest-neighbor-chains) suggests a large relaxation on placing an interstitial atom half-way between nearest neighbors, and indeed it is found that less energy is required to place an interstitial atom in such a position than in the more obvious face-centered position, though the latter is a position of lower potential when we ignore relaxation.

The Ewald potential at the center of a cube face is about $-0.34\ e/a$. By allowing the two nearest ions to move after having dropped a positive ion in the face center, we gain an additional relaxation energy of $0.381\ e^2/a$. On the other hand, the potential at the half-way point between nearest neighbors is calculated by the Ewald method to be only $-0.200\ e/a$, but allowing two atoms on either side along the 1:1:1 axis to relax we gain $0.535\ e^2/a$ in relaxation energy.

By allowing more atoms along the chain to relax simultaneously, we approach a relaxation energy which is nearly maximal for a "crowdion" of the form shown in Fig. 1. Each of the pair of ions nearest to the interstitial ion is displaced by an amount $p_1=\frac{1}{4}\sqrt{3}a$ along the line, $p_2=0.30a$, $p_3=0.2a$, $p_4=p_5\cdots=0$. The relaxation energy associated with this formation was calculated to be $-0.69\ e^2/a$ using the exact Ewald potential rather than the constant curvature approximation for p_1 (the latter giving too low a potential rise). The highest relaxation calculated by an approximate method (for a slightly different formation) was $-0.71\ e^2/a$.

However, the corresponding energy required for the formation of a vacancy is $+1.820-0.310=1.510\ e^2/a$, the relaxation being approximately the same ($0.310\ e^2/a$) whether we allow chain, or symmetric nearest neighbor, relaxation of 8 atoms.

Instead of creating the vacancy in the interior, we can, however, remove the positive ion from the surface of the crystal. In order to work out, then, the energy required to transfer a positive ion from the surface to an interstitial position half-way between nearest neighbors we shall make use of the empirical data relating to work function, ionization, and sublimation, giving us the work required to remove a positive ion from the surface to infinity.

The heat of sublimation of sodium at 20° was taken to be[7] 25.7 kcal./g-atom = 1.12 ev/g-atom. The ionization energy is 5.12 ev, and the empirical value taken for the work function[8] is 2.25 ev. We thus arrive at the value I for the energy required to remove a positive ion from the surface to infinity outside the crystal: $I=1.12+5.12-2.25=3.99$ ev. Allowing for errors in the experimental values, we take[9] $I=4.0\pm0.2$ ev.

In order to calculate the work required to bring a positive ion from infinity outside the crystal across the surface to an interstitial position in the interior of our lattice (thus standardizing our Ewald potentials to zero at infinity outside the crystal), we shall use an approximation[10] to our model of the crystal by considering it to

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[7] W. Edmondson and A. Egerton, Proc. Roy. Soc. **A113**, 520 (1926).

[8] R. J. Maurer, Phys. Rev. **57**, 653 (1940).

[9] This shows that removal of one of the surface ions involved demands almost exactly half the energy required for removal of an interior lattice ion.

[10] The quality of this approximation is shown by F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1950), p. 364.

be made up of spheres of uniform negative charge density surrounding the positive lattice points, the volume of each sphere being equal to the volume of the polygon corresponding to each lattice point, the total charge of the sphere being of course normalized to unit electronic charge. We shall also use the Bardeen[11] correction to allow for electron redistribution at the surface of sodium.

The volume of the unit (polygonal) cell in a b.c.c. lattice is $4a^3$. The radius of a sphere of equal volume is given by $R=(3/\pi)^{\frac{1}{3}}a$. The potential at the center of such a sphere of uniform charge density normalized to $-e$ is $-1.5(3/\pi)^{-\frac{1}{3}}e/a=-1.524\, e/a$. On the other hand, we had calculated this self-potential by the Ewald method to be $-1.820\, e/a$. Thus, to standardize all Ewald potentials to zero at infinity outside the crystal, one must add $+0.30\, e/a$ to their values. In particular, the potential at the point midway between nearest neighbors is therefore $-0.20+0.30=+0.10\, e/a$, and the energy gained in bringing the positive ion from infinity to that position is $-0.10+0.70$ (relaxation) $=0.60\, e^2/a$.

Allowing for a redistribution of electronic charge at the surface of the crystal (compared to the interior) resulting in an average dipole of 0.15 ev, as calculated by Bardeen, the net energy required to remove a positive ion from the surface to form a crowdion in the interior is given by

$$4.15 \text{ ev}-0.60\, e^2/a=0.61\, e^2/a-0.60\, e^2/a =0.01\pm 0.03\, e^2/a.$$

Thus the activation energy of formation for crowdions in sodium is less than 0.3 ev.

For the higher alkali metals the work function is practically the same, and the decreases in ionization and sublimation energy more than compensate the effect of the increase in interatomic distance on the relaxation and potential terms, so that we would expect a still lower activation energy of formation for crowdions (not taking into account the Bardeen correction).[12] In the case of lithium, the increase in ionization energy is small, the change in cell constant is more important, and we again expect a lower energy of formation for crowdions.

The activation energy associated with migration of such crowdions is small. Even for crowdions extending over only $4\cdot 3^{\frac{1}{2}}a$, the difference in energy between the symmetric position considered above, and the configuration obtained by shifting the crowdion (whose amplitude of displacement is taken to vary linearly over its length) rigidly through half a spacing (*viz.* $3^{\frac{1}{2}}a/n$), is found to be only $0.05\, e^2/a$ ($=0.3$ ev for sodium).[13] The energy of creation calculated above, referring as it does to the position of the crowdion on the potential hump, is the total energy of activation (the unit jump for an atom being $3^{\frac{1}{2}}a/n$ in length, where na is the length of the crowdion).

The picture we arrive at is then as follows: Crowdions extending over about eight spacings are formed by the motion of ions situated initially at surface ledges and subject to Brownian collisions from one side. These crowdions travel rapidly along nearest-neighbor axes throughout the crystal. As the crowdion flies in a straight line and cannot turn corners without considerable additional activation energy, we might expect anisotropy under suitable conditions. For very large single crystals we might expect time effects such as freezing in of equilibrium concentrations on rapid cooling. Moreover, it might be possible to inhibit the formation of crowdions at the surface by non mobile layers of foreign atoms. Foreign atoms in the interior of the lattice would not benefit preferentially by such a diffusion mechanism. Finally, as in the case of interstitial atoms, vacancies, and any other configurations assumed to exist under conditions where equilibrium concentrations are maintained, there is the possibility of detectable material flow under stationary temperature gradient conditions, though in this case a concentration gradient of crowdions is expected to be limited by an accompanying potential gradient.

For sufficiently low activation energy of migration, crowdions (which can be assigned definite mass) can be considered as particles with one degree of freedom of motion, and hence contribute to the specific heat and heat-conductivity.[14]

I wish to express my gratitude to Professor C. Zener for his helpful advice at all times.

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[11] J. Bardeen, Phys. Rev. **49**, 653 (1936).

[12] However, our electrostatic model of the crystal becomes increasingly unreliable for the higher alkali metals.

[13] Compare the similarly low energy of activation of migration (0.5 ev) calculated by Huntingdon and Seitz (reference 2) for an ordinary interstitialcy in copper.

[14] The kinematics of non-stationary "slip-waves" have been worked out for a different model (involving nearest-neighbor elastic interactions along the chain) by J. Frenkel and T. Kontorova, J. Phys. (USSR) **1**, 137 (1939).